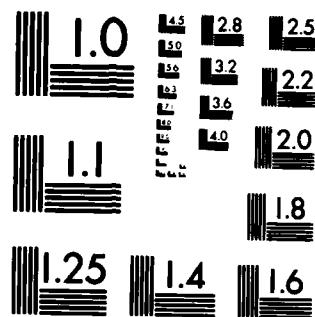


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The Electrochemistry of Polyacetylene:

Application in High Power Density Rechargeable Batteries

by

A. G. MacDiarmid, M. Aldissi, R. B. Kaner,

M. Maxfield, and R. J. Mammone

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University of Pennsylvania
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Philadelphia, Pennsylvania, 19104

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The best overall performance of rechargeable batteries using polyacetylene as both anode- and cathode-active materials are obtained from cells having a neutral (CH_x) cathode and n-doped anode in the charged state. It has been found that it is possible to chemically and electrochemically p-dope (CH_x) to the metallic regime in aqueous solution.		

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THE ELECTROCHEMISTRY OF POLYACETYLENE: APPLICATION

IN HIGH POWER DENSITY RECHARGEABLE BATTERIES:

by A. G. MacDiarmid, M. Aldissi, R. B. Kaner,

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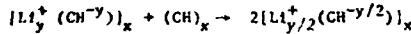
The fact that $(CH)_x$ film can be oxidized and reduced in reversible electrochemical reactions makes it an interesting material to study as a potentially useful electroactive material.

(1) RECHARGEABLE BATTERIES USING $(CH)_x$ FILM AS ELECTRODES^{1,2}

Four chief type of batteries employing $(CH)_x$ electrodes have been studied:

- (1) p-doped $(CH)_x$ cathode plus Li anode.
- (2) neutral $(CH)_x$ cathode plus Li anode.
- (3) p-doped $(CH)_x$ cathode plus n-doped $(CH)_x$ anode.
- (4) neutral $(CH)_x$ cathode plus n-doped $(CH)_x$ anode.

In so far as overall performance is concerned type (4) above is the best all-polymer cell so far developed. Since both neutral and reduced $(CH)_x$ have good stability in an electrolyte of 1M LiClO₄ in tetrahydrofuran a voltaic cell can be constructed using $(CH)_x$ as the cathode and (CH^{-y}) as the anode. During discharge the (CH^{-y}) gives up an electron to the $(CH)_x$ producing the net overall reaction:



where Li acts as the counter cation to stabilize the polycarbonion species. A cell of this type using 1/2 electrochemically reduced $(CH)_x$ for the anode and neutral $(CH)_x$ for the cathode has a potential of ~ 1.0V and a short circuit current of ~ 3mA/cm² of $(CH)_x$. The cells shows excellent stability, losing only ~ 0.02V during a six month period. They are fully rechargeable with coulombic efficiencies >99%. They are the first stable, rechargeable batteries developed in which both the cathode and anode active materials are organic polymers.

(2) AQUEOUS ELECTROCHEMISTRY OF $(CH)_x$

When trans- $(CH)_x$ film is p-doped i.e., oxidized by bromine, arsenic pentafluoride, etc. its conductivity increases by ca. eight orders of magnitude and it is converted to an "organic metal" having all the electronic properties of a conventional metal. All such p-doped material is, however, decomposed by water. Until the present study was undertaken the only apparent exception to this water instability involved the electrochemical p-doping of a piece of $(CH)_x$ film when it was placed in an aqueous 0.5M solution of KI and was attached to the positive terminal of a 9V dry cell, the other terminal being attached to a platinum counter electrode immersed in the solution. Doping took place in a few minutes to give $(CH_{10.07})_x$ having a conductivity in the metallic regime. The sum of the elemental analyses for C, H, and I was 99.8%. This showed that no reaction with water, to incorporate oxygen into the $(CH)_x$ had taken place. As time proceeded, we began to believe that the analysis must have been in error, and that oxygen surely must have been incor-

porated during the doping process. However, very recently the experiment was repeated (at a smaller voltage) and similar results were obtained. The non-aqueous electrochemistry of $(CH)_x$ has now been extended to another system as described below.

A piece of $(CH)_x$ film (2 cm x 2 cm) and a piece of Pt foil were placed in a saturated solution ~ 0.5M NaAsF₆ in 50% aqueous HF. The $(CH)_x$ was attached to the positive electrode and the Pt to the negative electrode respectively of a d.c. power supply. A constant potential of 1.0V was applied between the electrodes for ~ 30 minutes and the film was then washed in 50% HF and pumped in the vacuum system for 18 hours. In several different experiments, carried out under slightly different conditions, flexible, golden films having good metallic conductivity (ca. 10 to 100 $\Omega^{-1}cm^{-1}$) were obtained. It was most surprising to find that the films contained no oxygen. The F content varied from one preparation to another, e.g. $[CH^{+0.026}(AsF_5)_x]^{0.026}_x$; $(C+H+As+F = 100.2\%)$ and $[(CH^{+0.029}(AsF_4)_x]^{0.029}_x$; $(C+H+As+F = 100.3\%)$.

The nature of the dopant species and the cause of the variable F content is currently being investigated. It is believed that the dopant probably consists of a mixture of the $(AsF_6)^-$ and $(AsF_4)^-$ ions. The fact that $(CH)_x$ can be doped to the metallic regime either with iodine or with arsenic-fluorine species without the inclusion of oxygen is most surprising in view of the fact that p-doped $(CH)_x$ is believed to consist of polycarbonium ions. It is possible that the extent of delocalization of the positive charge is so great that, at least in certain cases, nucleophilic attack of the positive carbon atoms by water does not occur. Whatever the reason for the unexpected stability, these observations open up a whole new area of aqueous chemistry for conducting polymers.

The present results suggest that electrochemical studies not only of $(CH)_x$ but also of other conducting polymers represent an extensive area for further research not only of fundamental scientific interest but also of possible potential technological value.

ACKNOWLEDGEMENTS

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REFERENCES

- (1) A.G. MacDiarmid and A.J. Heeger, *Synth. Met.*, 1, 101 (1979/80); A.J. Heeger and A.G. MacDiarmid in *The Physics and Chemistry of Low Dimensional Solids*, ed. L. Alcacer (D. Reidel Publishing Co., Dordrecht, Holland, 1979).
- (2) P.J. Nigrey, A.G. MacDiarmid and A.J. Heeger, *J. Chem. Soc., Chem. Commun.*, 594 (1979); P.J. Nigrey, D. MacInnes, Jr., D.P. Nairns, A.G. MacDiarmid and A.J. Heeger in "Conducting Polymers", R.B. Seymour, Editor, p.227, Plenum Publishing Corp., New York (1981); P.J. Nigrey, D. MacInnes, Jr., D.P. Nairns, A.G. MacDiarmid, and A.J. Heeger, *J. Electrochem. Soc.*, 128, 1651 (1981); K. Kaneko, M. Maxfield, D.P. Nairns, A.G. MacDiarmid and A.J. Heeger, *J. Chem. Soc. Faraday Trans.*, in press (1982).
- (3) P.J. Nigrey, A.G. MacDiarmid, and A.J. Heeger, *J.C.S. Chem. Commun.*, 594 (1979).

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